

Ab Initio Molecular Orbital Calculations of 3,4-Dihydro-1,2-dioxin, 3,6-Dihydro-1,2-dioxin, 4*H*-1,3-Dioxin (1,3-Diox-4-ene), and 2,3-Dihydro-1,4-dioxin (1,4-Dioxene)

FILLMORE FREEMAN,¹ CHOONSUN LEE,¹ WARREN J. HEHRE,^{1,2} HENRY N. PO³

¹ Department of Chemistry, 516 Physical Sciences I, University of California, Irvine, California 92697-2025

² Wavefunction, Inc., Irvine, California

³ Department of Chemistry, California State University, Long Beach, California

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ABSTRACT: Optimized geometries and total energies for 3,4-dihydro-1,2-dioxin (**1**), 3,6-dihydro-1,2-dioxin (**2**), 4*H*-1,3-dioxin (1,3-diox-4-ene, **3**), and 2,3-dihydro-1,4-dioxin (1,4-dioxene, **4**) were calculated using *ab initio* 3-21G, 6-31G*, and MP2/6-31G*//6-31G* methods. The half-chair conformers of **1** (*C*₁), **2** (*C*₂), **3** (*C*₁), and **4** (*C*₂) are more stable than their respective planar structures [**1** (*C*_s), **2** (*C*_{2v}), **3** (*C*_s), and **4** (*C*_{2v})]. Among the four isomers **1–4**, the half-chair conformer of **3** is the most stable. It is 53.1, 54.6, and 3.4 kcal mol^{−1} more stable than **1**, **2**, and **4**, respectively. The largest energy difference (19.0 kcal mol^{−1}) is observed between the half-chair and planar conformers of **2**. The boat conformers of **2** and **4** are less stable than their respective half-chair conformers, but are more stable than their planar structures. Hyperconjugative orbital interactions (anomeric effects) contribute to the greater stability of **3** (*n*_{O(3)} → $\sigma^*_{C(2)-O(1)}$, *n*_{O(3)} → $\sigma^*_{C(2)-H_{ax}}$, *n*_{O(1)} → $\sigma^*_{C(2)-H_{ax}}$) and of **4** (*n*_{O(1)} → $\sigma^*_{C(2)-H_{ax}}$). The *ab initio* calculated structural features of the half-chair conformations of the dihydrodioxins **1–4** are compared with the half-chair conformations of cyclohexene and the chair conformations of cyclohexane, oxacyclohexane (tetrahydropyran), 1,2-dioxacyclohexane (1,2-dioxane), 1,3-dioxacyclohexane (1,3-dioxane), and 1,4-dioxacyclohexane (1,4-dioxane) © 1997 by John Wiley & Sons, Inc. *J Comput Chem* **18**: 1392–1406, 1997

Correspondence to: F. Freeman; e-mail ffreeman@uci.edu

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Introduction

Information concerning the properties of the 1,4-endoperoxides 3,4-dihydro-1,2-dioxin (1) and 3,6-dihydro-1,2-dioxin (2), and 4*H*-1,3-dioxin (1,3-diox-4-ene, 3) and 2,3-dihydro-1,4-dioxin (1,4-dioxene, 4) is of considerable spectroscopic,¹⁻⁹ synthetic,^{10,11} and theoretical^{12,13} interest owing to their chemistry and to their unique molecular structures. Electron diffraction,¹⁴⁻¹⁶ microwave,^{14,15,17} and other spectroscopic studies of the molecular geometry of cyclohexene have concluded that the half-chair conformer (four coplanar carbon atoms, C_2) (Fig. 1) is more stable than the boat.¹⁴⁻²⁰ It is of interest to examine the stereoelectronic effects and to observe the effects on molecular geometry by replacing two methylene groups in cyclohexene with oxygen atoms.²¹⁻²³ It is expected that introduction of two oxygen atoms into cyclohexene would lead to a modified (distorted) half-chair or boat conformation to accommodate the shorter C—O bond lengths (1.43 Å relative to a C—C value of 1.54 Å).²⁴⁻²⁶ Similar effects on the chair conformation are expected from introduction of two oxygen atoms into cyclohexane (Fig. 1).^{14,15,27}

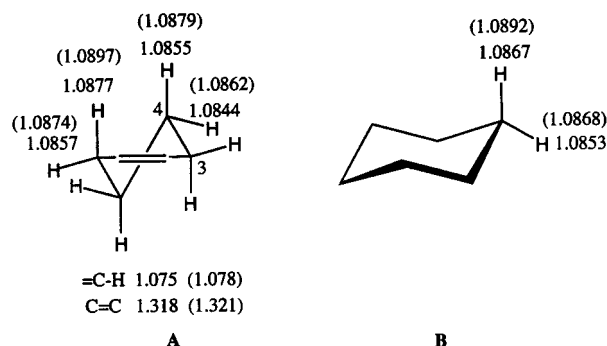
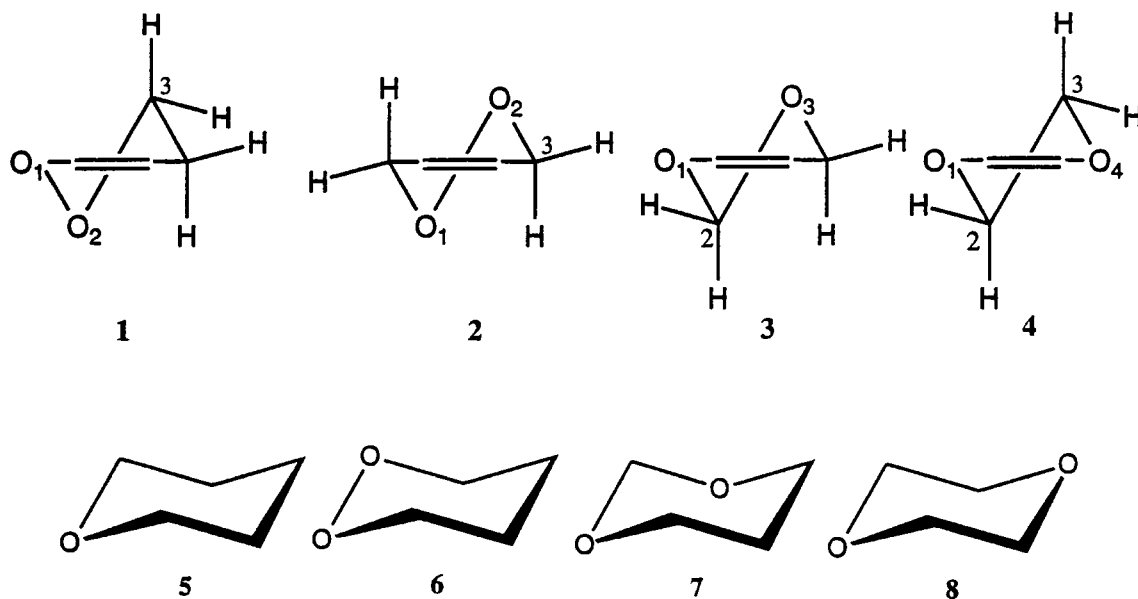


FIGURE 1. Calculated (3-21G) bond distances (Å) for cyclohexene (A) and cyclohexane (B). The 6-31G* bond distances (Å) are given in parentheses.

The present study was undertaken to: (1) explore the *ab initio* calculated energies and structures of the more stable conformers of the isomeric dihydrodioxins 1-4; (2) to compare and contrast the *ab initio* calculated energies and structures of 1-4, cyclohexene, cyclohexane, oxacyclohexane (tetrahydropyran, 5), 1,2-dioxacyclohexane (1,2-dioxane, 6), 1,3-dioxacyclohexane (1,3-dioxane, 7), and 1,4-dioxacyclohexane (1,4-dioxane, 8); and (3) to explore the possibility of anomeric effects (hyperconjugative interactions) and other stereoelectronic effects in 1-4.



Computational Methodology

The total energies and optimized geometries for the four isomers 3,4-dihydro-1,2-dioxin (**1**), 3,6-dihydro-1,2-dioxin (**2**), 4*H*-1,3-dioxin (**3**), and 2,3-dihydro-1,4-dioxin (**4**) have been calculated at *ab initio* 3-21G, 6-31G* and MP2/6-31G*//6-31G* molecular orbital levels using the SPARTAN 4.0 quantum mechanical program.^{28–30} Geometry optimizations using the 3-21G²⁸ and 6-31G*²⁹ basis sets and single point MP2/6-31G*//6-31G* energy calculations were carried out for the planar and the half-chair conformers of each isomer (**1–4**).¹² The 3-21G geometrical parameters are used in the discussion throughout because it is known that the 6-31G* basis set underestimates single bond lengths involving electronegative first-row atoms.^{31–34} Calculations for the boat conformations of **2** and **4** were also done for comparison. In the planar conformations, the dihedral angles (O—C=C—C, C=C—C—C, =C—C—C—O, C—O—O—C, O—O—C=C) were constrained to 0° to preserve symmetry during the calculations. Twist angles are obtained for the half-chair conformers (**1–4**) and are defined for each dihydrodioxin (Fig. 2). In **1** and in **2**, the twist angle is the angle formed by O(1)—O(2) and a triangular plane defined by C(3), C(4), and C(6). The twist angle in **3** is formed by C(2)—O(3) and a triangular plane defined by C(4), C(6), and O(1), and the twist angle in **4** is formed by C(2)—C(3) and a triangular plane defined by O(4), C(6), and O(1). No

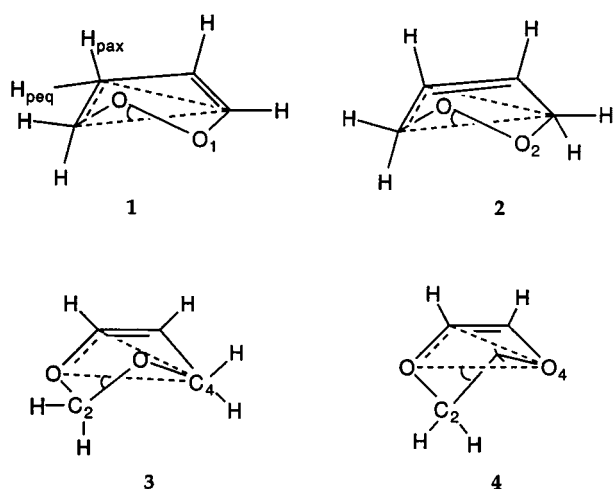


FIGURE 2. Twist angles for 3,4-dihydro-1,2-dioxin (**1**), 3,6-dihydro-1,2-dioxin (**2**), 4*H*-1,3-dioxin (**3**), and 2,3-dihydro-1,4-dioxin (**4**).

symmetry constraint was imposed on the 3-21G and 6-31G* minimal-energy conformations of cyclohexene, cyclohexane, oxacyclohexane (**5**), 1,2-dioxane (**6**), 1,3-dioxane (**7**), and 1,4-dioxane (**8**). 6-31G* and 6-31G** gave essentially the same values for cyclohexane. The pseudoaxial and pseudoequatorial hydrogens are indicated as H_{pax} and H_{peq} (cf. **1**).





Theoretical Consideration of Dihydrodioxins 1–4

The factors which primarily determine the relative stability of the conformers of dihydrodioxins **1–4** are angle strain, lone pair–lone pair repulsion, and torsional strain resulting from eclipsing of adjacent methylene groups. Dihydrodioxins **1** and **4** have one pair of adjacent methylene groups and dihydrodioxins **2** and **3** have no adjacent methylene groups. Table I shows that the respective half-chair conformers **1** (C₁), **2** (C₂), **3** (C₁), and **4** (C₂) of the isomeric dihydrodioxins are more stable than their respective planar conformers at the MP2/6-31G*//6-31G* level. The largest barrier to planarity (19.0 kcal mol^{−1}) is observed for 3,6-dihydro-1,2-dioxin (**2**). Among the isomeric dioxins **1–4**, the half-chair conformer of 4*H*-1,3-dioxin (**3**) is the most stable. It (**3**) is 53.1, 54.6, and 3.4 kcal mol^{−1} more stable than **1**, **2**, and **4**, respectively. The half-chair conformer of **1** is 1.6 kcal mol^{−1} more stable than that of **2**.

In addition to the half-chair and planar conformations, dioxins **2** and **4** may also exist in their respective boat conformations (C_s) (Fig. 3; Table II). At the MP2/6-31G*//6-31G* level, the boat conformer of **2**, which is less stable than the boat conformer of **4**, is 12.3 kcal mol^{−1} less stable than its half-chair conformer and 6.7 kcal mol^{−1} more stable than the planar form. Similarly, the boat conformer of **4** is 10.6 kcal mol^{−1} less stable than the half-chair and 1.7 kcal mol^{−1} more stable than the planar form. The distance between the flag-pole hydrogens in the boat conformer of **2** is 2.584 Å, which is greater than the sum of their van der Waal radii. The distance between the oxygens in the boat conformer of **4** is 2.747 Å, which is less than the sum of their van der Waal radii (Fig. 3).

The barriers to conformational inversion of the half-chair structures in **1–4** are the lowest energy pathways between the two possible half-chair conformers. The top of the barrier may occur at the

TABLE I.
Comparison of Calculated Energies of Dihydrodioxins 1 – 4.

| Dihydrodioxin | Half-Chair Conformation (C ₁ or C ₂) | | | Planar Conformation (C _s or C _{2v}) | | | Energy Differences $\Delta E = E_{\text{half-chair}} - E_{\text{planar}},^{a-e}$ (kcal mol ⁻¹) | | |
|--|--|--|--|---|--|---|--|--------|--------------------|
| | 3-21G | 6-31G* | MP2/6-31G*//6-31G* | 3-21G | 6-31G* | MP2/6-31G*//6-31G* | 3-21G | 6-31G* | MP2/6-31G*//6-31G* |
|  1 | C ₁ -302.876826 ΔE = 50.2 | C ₁ -304.552754 ΔE = 59.3 | C ₁ -305.416769 ΔE = 53.1 | C _s -302.856734 ΔE = 56.4 | C _s -304.5319695 ΔE = 63.7 | C _s -305.393984 ΔE = 56.3 | 12.6 | 13.0 | 14.3 |
|  2 | C ₂ -302.87669 ΔE = 50.2 | C ₂ -304.552961 ΔE = 59.2 | C ₂ -305.414259 ΔE = 54.6 | C _{2v} -302.850199 ΔE = 60.6 | C _{2v} -304.5254533 ΔE = 67.8 | C _{2v} -305.383975 ΔE = 62.6 | 16.6 | 17.3 | 19.0 |
|  3 | C ₁ -302.956753 ΔE = 0.00 | C ₁ -304.647264 ΔE = 0.00 | C ₁ -305.501305 ΔE = 0.00 | C _s -302.946696 ΔE = 0.00 | C _s -304.6335244 ΔE = 0.00 | C _s -305.483666 ΔE = 0.00 | 6.3 | 8.6 | 11.1 |
|  4 | C ₂ -302.948899 ΔE = 4.9 | C ₂ -304.638875 ΔE = 5.3 | C ₂ -305.495900 ΔE = 3.4 | C _{2v} -302.933269 ΔE = 8.4 | C _{2v} -304.6231763 ΔE = 6.5 | C _{2v} -305.476373 ΔE = 4.6 | 9.8 | 9.9 | 12.3 |

^aOne hartree is 627.51 kcal mol⁻¹.
^bAll energy differences (ΔE, kcal mol⁻¹) are calculated at the MP2/6-31G*//6-31G* level. The half-chair conformation of 4H-1,3-dioxin (**3**) is 53.1, 54.6, and 3.4 kcal mol⁻¹ more stable than the half-chair conformers of **1**, **2**, and **4**, respectively.
^cΔE = E₁ - E₂ = 1.6 kcal mol⁻¹ (half-chair structures).
^dΔE = E₃ - E₂ = 54.6 kcal mol⁻¹ (half-chair structures).
^eΔE = E₃ - E₄ = 3.4 kcal mol⁻¹ (half-chair structures).

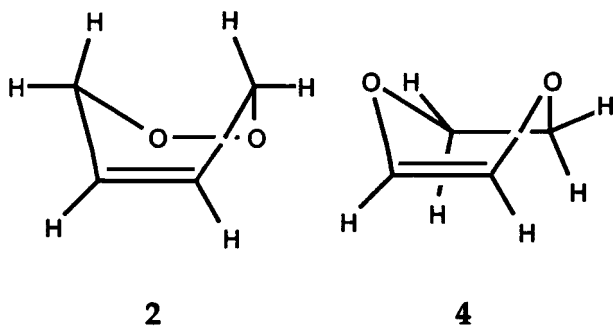


FIGURE 3. Boat conformations of 3,6-dihydro-1,2-dioxin (**2**) and 2,3-dihydro-1,4-dioxin (**4**).

boat, planar, or some other conformation. For dihydrodioxins **1** and **3**, the barrier to conformational inversion between the two possible half-chair conformers may be the barrier to planarity, which is the energy difference between the half-chair and planar structures. The barrier to interconversion between the two respective half-chair conformers of dihydrodioxins **2** and **4** may be the energy difference between their respective boat and half-chair conformers, because the boat structures are of lower energy than the planar structures.^{3,26}

3,4-DIHYDRO-1,2-DIOXIN (**1**)

At the MP2/6-31G*//6-31G* level, the half-chair conformer of **1** is of lower energy (14.3 kcal mol⁻¹; Table I) than its planar structure (*C_s*) owing to smaller eclipsing of the adjacent methylene groups and to the lower repulsive interactions among the nonbonded electrons on the vicinal oxygen atoms. To alleviate lone pair–lone pair repulsion, **1** adopts the half-chair conformation with a twist angle of 28.2° (3-21G; Fig. 4; Table III). Twisting of the ring reduces both the angle strain and torsional strain by decreasing the inner angles and staggering the methylene groups. The 3-21G-calculated =C(6)—O—O and C(3)—O—O bond angles are 110.0° and 106.8°, respectively. The H_{ax}—C(3)—C(4)—H_{pax}, H—C=C—H, C(3)—C(4)—C(5)=C(6), C(4)—C(5)=C(6)—O(1), and C—O—O—C torsion angles in the half-chair conformation of **1** are 164.4°, 2.4°, 10.5°, 0.7°, and 58.9°, respectively. The calculated torsion angle in **1** for C(4)—C(5)=C(6)—O(1) of 0.7° is similar to the calculated value of 0.9° for C—C=C—C in cyclohexene. In cyclohexene, the C(4)—H_{ax} and the C(3)—H_{pax} bond lengths are longer than the corresponding C(4)—H_{eq} and C(3)—H_{peq} bonds (Fig. 1). In **1**, the respective axial

TABLE II. Comparison of Calculated Energies of Conformers of 3,6-Dihydro-1,2-dioxin (**2**) and 2,3-Dihydro-1,4-dioxin (**4**).

| | Energy, Hartree ^a | | | Energy, Hartree | | Δ <i>E</i> -Energy Differences, kcal mol ⁻¹ | | |
|---------------|------------------------------|-------------|--------------------|---------------------------------|------------------------------|---|---|--|
| | Boat Conformation | | | Conformation | | | | |
| | <i>C_s</i> | 6-31G* | MP2/6-31G*//6-31G* | Half-Chair <i>C₂</i> | Planar <i>C_{2v}</i> | <i>E</i> _{half-chair} — <i>E</i> _{boat} | <i>E</i> _{boat} — <i>E</i> _{planar} | |
| Dihydrodioxin | 3-21G | 6-31G* | MP2/6-31G*//6-31G* | MP2/6-31G*//6-31G* | MP2/6-31G*//6-31G* | MP2/6-31G*//6-31G* | MP2/6-31G*//6-31G* | |
| | –302.856777 | –304.531678 | –305.394676 | –305.414259 | –305.383975 | 12.3 | 6.7 | |
| | –302.934188 | –304.624930 | –305.479075 | –305.495900 | –305.476373 | 10.6 | 1.7 | |

^aOne hartree is 627.51 kcal mol⁻¹

and equatorial and the pseudoaxial and pseudoequatorial C—H bonds are of comparable lengths (Fig. 4). The 3-21G-calculated C=C bond distances in cyclohexene and **1** are 1.318 Å and 1.311 Å, respectively. The 3-21G-calculated C(6)—O, C(3)—O, and O—O bond distances in **1** are 1.403, 1.464, and 1.463 Å, respectively (Fig. 4, Table III in the Supplementary Material).^{12,31–34} The 3-21G-calculated dipole moment for **1** is 3.3 debyes and Figure 4 shows the calculated electrostatic charges for **1**.

3,6-DIHYDRO-1,2-DIOXIN (**2**)

Microwave and ¹H NMR spectroscopy established the conformation of 3,6-dihydro-1,2-dioxin (**2**) to be half-chair.^{5–7,12,14,15} At the MP2/6-31G*//6-31G* level, the half-chair conformation of **2** is 19.0 kcal mol^{–1} more stable than the planar conformation and 12.3 kcal mol^{–1} more stable than the boat form (Tables I and II).^{7,35} The stability of the half-chair conformer of **2** is attributed to its ability to reduce the σ – π lone-pair electron repulsion on the vicinal oxygen atoms by twisting to make the lone pair electrons orthogonal to each other. The optimized structure calculated for **2** with the 3-21G basis set is in good agreement with microwave and photoelectron spectroscopic studies.^{5–7,12,14,15,31–34,36–39} The C—O—O bond angles calculated at the 3-21G level for half-chair **2**, planar **2**, and boat **2** are 105.0°, 120.2°, and 114.2°, respectively. The calculated C—C=C—C torsion angle in half-chair **2** (3.8°) is larger than the calculated C—C=C—C torsion angle in cyclohexene (0.9°). Dihydrodioxin **2** has a C—O—O—C torsion angle of 79.7° which is close to 90° because the adjacent oxygen atoms have a strong preference for orthogonality to reduce the lone-pair electron repulsion.

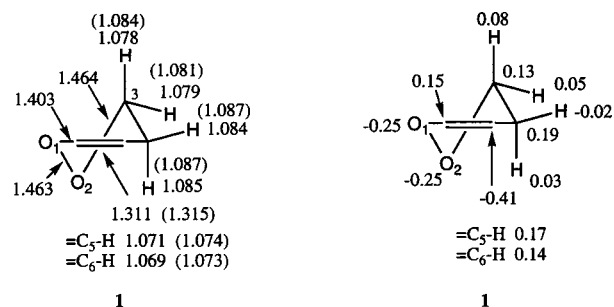


FIGURE 4. Calculated (3-21G) bond distances (Å) and electrostatic charges (electron) for 3,4-dihydro-1,2-dioxin (**1**). The 6-31G* bond distances (Å) are given in parentheses.

The C—O—O—C torsion angle of 79.7° for **2** is the largest among the dihydrodithins **1–4**. In hydrogen peroxide, the experimental value of the H—O—O—H torsion angle is 111.5°. ^{40–42} Also, the 3-21G-calculated C—O—O—C torsion angle (79.7° vs. 80 ± 2°) and the twist angle (39.0° vs. 38.3°) compare favorably with microwave studies.^{5–7,14,15} The twist angle in **2** is larger than those in **1** (28.2°), in cyclohexene (30.1°),^{17,38,39} and in 3,6-dihydro-2H-pyran (31.5°).¹ In **2**, as in **1**, the respective axial and equatorial and the pseudoaxial and pseudoequatorial C—H bonds are of comparable lengths (Fig. 5). The 3-21G-calculated C=C, Csp³—O, and O—O bond lengths in **2** are 1.313 Å, 1.454 Å, and 1.464 Å, respectively (Fig. 5; Table IV).^{12,31–34} Figure 5 also shows the calculated electrostatic charges for **2**.

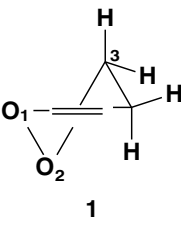
At the MP2/6-31G*//6-31G* level, planar **1** is 6.3 kcal mol^{–1} more stable than the planar conformer of **2**. The half-chair conformer of **1** is more stable than the half-chair conformer of **2** by 1.6 kcal mol^{–1} at the MP2/6-31G*//6-31G* level. This difference in energy results from a complex interplay of stereoelectronic and structural effects. Although an interaction between the oxygen nonbonded electrons and the π -bond electrons of the ethenyl ether double bond is destabilizing, an interaction between the oxygen nonbonded electrons and π^* is stabilizing. The 3-21G optimized C—O—O—C dihedral angles for the half-chair conformations of **1** (59.86°) and of **2** (79.7°) suggest that the interaction between nonbonded electrons and π -bond electrons in **1** may override the increased repulsive interaction between the closer oxygen lone pairs and results in a smaller C—O—O—C torsion angle in **1** than in **2**.

4H-1,3-DIOXIN (1,3-DIOX-4-ENE, **3**)

The half-chair conformation of **3**, in which the oxygen atoms are separated by a methylene group, is the most stable of the dihydrodioxins **1–4** and has the smallest difference (11.1 kcal mol^{–1}) between its half-chair and planar structures (Table I; Table V).^{3,4,8,27j} The 3-21G-calculated twist angle of 27.9° (Table V) for **3** is close to the angle of 30.9° predicted by MM2 calculations^{3,26} and smaller than the angle of 33.2° determined from vibrational potential energy surfaces.^{3,14,15} The C=C bond length in **3** is 1.314 Å, which is close to the calculated value of 1.318 Å for cyclohexene.

The greater stability of **3** relative to **1**, **2**, and **4** may be due to the absence of adjacent methylene groups and to hyperconjugative orbital interac-

TABLE III.
Calculated Dipole Moment and Geometry for 3,4-Dihydro-1,2-dioxin (1).



| | C ₁ Half-Chair | | C _s , Planar | |
|---|---------------------------|--------|-------------------------|--------|
| | 3-21G | 6-31G* | 3-21G | 6-31G* |
| Bond length (Å) | | | | |
| O ₁ —O ₂ | 1.463 | 1.391 | 1.462 | 1.394 |
| O ₂ —C ₃ | 1.464 | 1.411 | 1.483 | 1.429 |
| C ₃ —C ₄ | 1.532 | 1.523 | 1.547 | 1.536 |
| C ₄ —C ₅ = | 1.511 | 1.504 | 1.497 | 1.492 |
| C ₅ =C ₆ | 1.311 | 1.315 | 1.306 | 1.311 |
| =C ₆ —O ₁ | 1.403 | 1.360 | 1.382 | 1.343 |
| =C ₅ —H | 1.071 | 1.074 | 1.070 | 1.073 |
| =C ₆ —H | 1.069 | 1.073 | | |
| C ₃ —H _{pax} | 1.078 | 1.084 | 1.078 | 1.082 |
| C ₃ —H _{peq} | 1.079 | 1.081 | | |
| C ₄ —H _{pax} | 1.085 | 1.087 | | |
| C ₄ —H _{peq} | 1.084 | 1.087 | | |
| Bond angle (°) | | | | |
| O ₁ —O ₂ —C ₃ | 106.8 | 109.7 | 120.0 | 121.7 |
| O ₂ —C ₃ —C ₄ | 108.5 | 109.3 | 119.0 | 118.8 |
| C ₃ —C ₄ —C ₅ = | 109.0 | 107.9 | 113.3 | 112.5 |
| C ₄ —C ₅ =C ₆ | 121.8 | 120.7 | 123.1 | 121.7 |
| C ₅ =C ₆ —O ₁ | 124.2 | 124.4 | 127.2 | 126.8 |
| =C ₆ —O ₁ —O ₂ | 110.0 | 111.8 | 117.5 | 118.5 |
| H—C ₃ —H | 110.4 | 109.2 | | |
| H—C ₄ —H | 108.0 | 107.1 | | |
| Torsion angle (°) | | | | |
| H _{ax} —C ₃ —C ₄ —H _{pax} | 164.4 | 161.8 | 118.5 | 117.4 |
| H _{eq} —C ₃ —C ₄ —H _{peq} | 79.2 | 79.5 | | |
| =C ₆ —O ₁ —O ₂ —C ₃ | 58.9 | 56.9 | 0 | 0 |
| C ₃ —C ₄ —C ₅ =C ₆ | 10.5 | 10.4 | 0 | 0 |
| O ₁ —O ₂ —C ₃ —C ₄ | 71.2 | 69.7 | | |
| O ₂ —C ₃ —C ₄ —C ₅ | 44.8 | 43.9 | | |
| C ₄ —C ₅ =C ₆ —O ₁ | 0.7 | 1.1 | | |
| C ₅ =C ₆ —O ₁ —O ₂ | 25.4 | 21.3 | | |
| H—C ₅ =C ₆ —H | 2.4 | 2.7 | | |
| Twist angle (°) | 28.2 | 24.7 | 0 | 0 |
| Dipole moment (debye) | 3.3 | 2.6 | 3.7 | 2.9 |

tions (anomeric effects).^{8,43–54} Although the anomeric effect has been studied extensively, its origin is still debated.⁵⁰ In one hypothesis (double bond/no bond model), there is a $n_{\text{O}} \rightarrow \sigma_{\text{C-H}_{\text{app}}}^*$ interaction between a pair of nonbonded electrons on oxygen and the axial [antiperiplanar (app)] adjacent C—H bond. Another proposal is that a

$\sigma_{\text{C-O}} \rightarrow \sigma_{\text{C-H}_{\text{eq}}}^*$ or a $\sigma_{\text{C-H}_{\text{eq}}} \rightarrow \sigma_{\text{C-O}}^*$ interaction, rather than a $n_{\text{O}} \rightarrow \sigma_{\text{C-H}_{\text{ax}}}^*$, can be operative. Oxygen has two lone-pair orbitals, one a high-energy p -type orbital that is perpendicular to the C—O—C plane in **3**, and a lower energy, sp^2 -type orbital. In **3**, the anomeric effect may be attributed to a favorable overlap between the high-energy

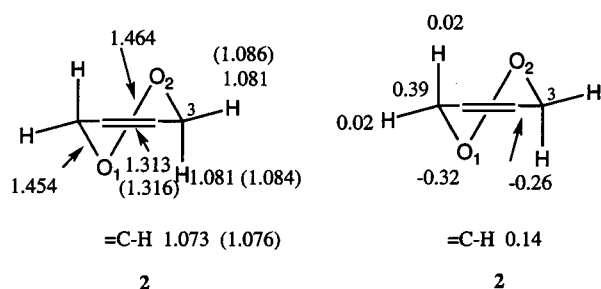


FIGURE 5. Calculated (3-21G) bond distances (Å) and electrostatic charges (electron) for 3,6-dihydro-1,2-dioxin (2). The 6-31G* bond distances (Å) are given in parentheses.

filled *p*-type lone pair on O(3) and the unfilled C(2)—O(1) or C(2)—H_{ax} antibonding σ^* orbital. This stabilizing $n_{O(3)} \rightarrow \sigma_{C(2)-O(1)}^*$ or $n_{O(3)} \rightarrow \sigma_{C(2)-H_{ax}}^*$ or anomeric hyperconjugation in **3** would be maximized in a conformation in which there is an antiperiplanar relationship between the *p*-type

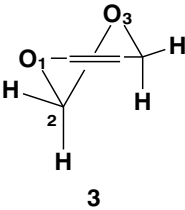
nonbonded electron pair on O(3) and the antiperiplanar C(2)—O(1) σ or C(2)—H_{ax} bond.^{8,49–51} These effects correctly anticipate a shortening (1.415 Å) of the C(2)—O(3) bond and a concomitant lengthening (1.433 Å) of the C(2)—O(1) or C(2)—H_{ax} (1.083 Å) bond (Fig. 6; Table V). The lengthening of the C(2)—O(1) bond may be diminished somewhat by an $n_{O(1)} \rightarrow \sigma_{C(2)-H_{ax}}^*$ anomeric interaction, and a $n_{O(1)} \rightarrow \sigma_{C(2)-H_{ax}}^*$ interaction may contribute to the lengthening of the C(2)—H_{ax} bond. The O(3)—C(4) single bond length of 1.450 Å in **3** is similar to the O(1)—C(6) single bond lengths of 1.454 Å and 1.444 Å in **2** and **4**, respectively.

The slightly longer C(4)—H_{pax} (1.085 Å) than C(4)—H_{peq} (1.080 Å) bond length suggest that there may be a $n_{O(3)} \rightarrow \sigma_{C(4)-H_{pax}}^*$ interaction in **3**. However, the O(3)—C(4) single bond length of 1.450 Å mitigates against such an interaction. In cyclohexene and cyclohexane the calculated C—H_{ax} bond lengths are slightly longer than the

TABLE IV. Calculated Dipole Moment and Geometry for 3,6-Dihydro-1,2-dioxin (2).

| <i>Ab initio</i> level | C ₂ , Half-Chair | | C _{2v} , Planar | | C _s , Boat | | Exptl ^{5–7} |
|--|-----------------------------|--------|--------------------------|--------|-----------------------|--------|----------------------|
| | 3-21G | 6-31G* | 3-21G | 6-31G* | 3-21G | 6-31G* | |
| Bond length (Å) | | | | | | | |
| O ₁ —O ₂ | 1.464 | 1.393 | 1.470 | 1.406 | 1.472 | 1.405 | 1.463 |
| C ₃ —C ₄ = | 1.508 | 1.504 | 1.493 | 1.489 | 1.504 | 1.502 | 1.504 |
| C ₄ =C ₅ | 1.313 | 1.316 | 1.306 | 1.310 | 1.313 | 1.315 | 1.338 |
| C ₆ —O ₁ | 1.454 | 1.404 | 1.460 | 1.410 | 1.466 | 1.411 | 1.426 |
| =C—H | 1.073 | 1.076 | 1.073 | 1.076 | 1.071 | 1.075 | 1.09 |
| C ₃ —H _{peq} | 1.081 | 1.084 | 1.083 | 1.086 | 1.079 | 1.081 | 1.10 |
| C ₃ —H _{pax} | 1.081 | 1.086 | | | | | |
| Bond angle (°) | | | | | | | |
| O ₁ —O ₂ —C ₃ | 105.0 | 107.6 | 120.2 | 121.6 | 114.2 | 115.8 | |
| C ₄ =C ₅ —C ₆ | 120.7 | 119.7 | 123.1 | 121.9 | 116.9 | 116.1 | 119.9 |
| =C ₅ —C ₆ —O ₁ | 109.8 | 110.2 | 116.8 | 116.6 | 111.7 | 112.0 | 110.3 |
| H—C ₃ —H | 109.7 | 108.5 | | | | | |
| Torsion angle (°) | | | | | | | |
| C ₆ —O ₁ —O ₂ —C ₃ | 79.7 | 78.4 | 0 | 0 | 0 | 0 | 80 ± 2 |
| C ₃ —C ₄ =C ₅ —C ₆ | 3.8 | 3.0 | 0 | 0 | 0 | 0 | |
| O ₁ —O ₂ —C ₃ =C ₄ | 57.1 | 55.3 | | | | | |
| O ₂ —C ₃ —C ₄ =C ₅ | 17.0 | 15.7 | | | | | |
| Twist angle (°) | 39.1 | 37.0 | 0 | 0 | 0 | 0 | 38.3 |
| Dipole moment (debye) | 3.2 | 2.7 | 4.1 | 3.5 | 4.0 | 3.4 | |

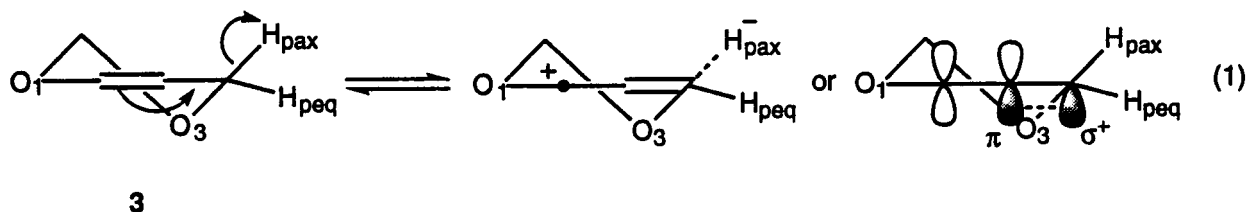
TABLE V.
Calculated Dipole Moment and Geometry for 4*H*-1,3-dioxin (**3**).



| | C ₁ , Half-Chair | | C _s , Planar | |
|--|-----------------------------|--------|-------------------------|--------|
| | 3-21G | 6-31G* | 3-21G | 6-31G* |
| Bond length (Å) | | | | |
| O ₁ —C ₂ | 1.433 | 1.398 | 1.437 | 1.403 |
| C ₂ —O ₃ | 1.415 | 1.377 | 1.421 | 1.386 |
| O ₃ —C ₄ | 1.450 | 1.408 | 1.446 | 1.407 |
| C ₄ —C ₅ = | 1.510 | 1.503 | 1.501 | 1.493 |
| C ₅ =C ₆ | 1.314 | 1.318 | 1.310 | 1.313 |
| =C ₆ —O ₁ | 1.383 | 1.351 | 1.374 | 1.344 |
| =C ₅ —H | 1.070 | 1.074 | 1.068 | 1.073 |
| =C ₆ —H | 1.068 | 1.073 | | |
| C ₂ —H _{pax} | 1.083 | 1.088 | 1.083 | 1.086 |
| C ₂ —H _{peq} | 1.072 | 1.076 | | |
| C ₄ —H _{pax} | 1.085 | 1.089 | | |
| C ₄ —H _{peq} | 1.080 | 1.082 | | |
| Bond angle (°) | | | | |
| H—C ₂ —H | 111.5 | 110.6 | | |
| H—C ₄ —H | 108.7 | 107.6 | | |
| O ₁ —C ₂ —O ₃ | 111.6 | 112.1 | 116.5 | 117.7 |
| C ₂ —O ₃ —C ₄ | 113.6 | 113.0 | 123.9 | 124.3 |
| O ₃ —C ₄ —C ₅ = | 110.6 | 110.1 | 113.6 | 113.3 |
| C ₄ —C ₅ =C ₆ | 120.9 | 119.9 | 121.3 | 120.4 |
| C ₅ =C ₆ —O ₁ | 123.4 | 123.1 | 124.4 | 124.4 |
| =C ₆ —O ₁ —C ₂ | 114.3 | 113.1 | 120.4 | 119.9 |
| Torsion angle (°) | | | | |
| H—C ₅ =C ₆ —H | 1.4 | 1.9 | | |
| O ₁ —C ₂ —O ₃ —C ₄ | 60.3 | 64.1 | 0 | 0 |
| C ₂ —O ₃ —C ₄ —C ₅ = | 40.7 | 41.7 | 0 | 0 |
| O ₃ —C ₄ —C ₅ =C ₆ | 8.8 | 8.8 | 0 | 0 |
| C ₄ —C ₅ =C ₆ —O ₁ | 4.6 | 4.2 | 0 | 0 |
| C ₅ =C ₆ —O ₁ —C ₂ | 13.6 | 15.1 | 0 | 0 |
| C ₆ —O ₁ —C ₂ —O ₃ | 45.2 | 48.6 | | |
| Twist angle (°) | 27.9 | 29.2 | 0 | 0 |
| Dipole moment (debye) | 2.1 | 1.8 | 1.4 | 1.1 |

C—H_{eq} bond distances (Fig. 1) and, in cyclohexene, the calculated C—H_{pax} bond lengths are longer than the C—H_{peq} bond distances. The double bond may exert an effect akin to the anomeric effect (double bond/no-bond resonance) at C(4) which would lengthen the C(4)—H_{pax} bond [eq. (1)]. This appears unlikely because the C=C bond length (1.314 Å), in **3** is comparable to the C=C

in cyclohexene (1.318 Å), **1** (1.311 Å), **2** (1.313 Å), and **4** (1.313 Å). Thus, in **3**, the $n_{O(3)} \rightarrow \sigma_{C(2)-O(1)}^*$ is probably the dominant anomeric interaction because σ_{C-O}^* is a more effective acceptor orbital than σ_{C-H}^* .⁵⁰ An opening of the O—C—O bond angle (111.5°) in **3**, relative to the normal tetrahedral value, is reasonable owing to the partial sp^2 character of the C(2) carbon atom.



The 3-21G calculated O(3)—C(4)—C(5)=C(6) and C(4)—C(5)=C(6)—O(1) torsion angles of 8.8° and 4.5°, respectively, suggest that **3** has a modified half-chair (sofa or bent-chair) conformation (Fig. 6).^{3,4,8} In a sofa or bent-chair conformation, five atoms are or are very nearly coplanar.^{27j}

2,3-DIHYDRO-1,4-DIOXIN (**4**)

The structure of 2,3-dihydro-1,4-dioxin (**4**) has been the subject of ¹H NMR,^{9,14,15,55,56} microwave,^{1,2} molecular mechanics,²⁶ far-infrared,^{3,57} and Raman^{3,58} studies, with the conclusion that its conformation is half-chair with an O—C—C—O torsion angle of 60° or 61°, which is similar to the calculated angle of 61.3° (Table VI). Far-infrared,³ microwave,^{1,2} and Raman³ studies show that the half-chair conformer of **4** is 11.0 and 11.8 kcal mol⁻¹ more stable than the respective boat and planar forms. The corresponding calculated values at the MP2/6-31G*/6-31G* level are 10.6 kcal mol⁻¹ and 12.3 kcal mol⁻¹ (Tables I and II). MM3 calculations²⁶ show that the half-chair conformation of **4** is 11.8 kcal mol⁻¹ more stable than the planar structure. The 3-21G computed dipole moment of **4** is 0.8 debye and the calculated twist angle is 29.49 (Table VI). The larger C—O—C bond angle of 113.5° in **4** may suggest that oxygen

nonbonding electrons may have 2*p*–2*p* π interactions with the carbon–carbon double bond. The C—O—C angle (111°) in dimethyl ether⁵⁹ increases to 120° in ethenyl methyl ether⁶⁰ and in methoxybenzene.⁶¹

The C(2)—H_{pax} bond length (1.082 Å) in **4** is longer than the C(2)—H_{peq} bond (1.077 Å) (Fig. 7). This suggests that the $n_{O(1)} \rightarrow \sigma_{C(2)-H_{pax}}^*$ is the dominant anomeric effect. Thus, it appears from these calculations that there are no anomeric effects in **1** and **2**, $n_{O(3)} \rightarrow \sigma_{C(2)-O(1)}^*$, $n_{O(3)} \rightarrow \sigma_{C(2)-H_{ax}}^*$, and $n_{O(1)} \rightarrow \sigma_{C(2)-H_{ax}}^*$ anomeric effects in **3** and $n_{O(1)} \rightarrow \sigma_{C(2)-H_{pax}}^*$ anomeric effect in **4**.

The half-chair conformers of **3** and **4** are at least 50 kcal mol⁻¹ more stable than the half-chair conformers of dihydrodioxins **1** and **2**. The half-chair conformer of 1,3-dioxene (**3**) is more stable than that of **4** by 3.4 kcal mol⁻¹. This energy difference may be rationalized in terms of repulsive interactions between nonbonded electrons on oxygens in **1** and **2**. In **4**, the two methylene groups separating the oxygen atoms reduce the lone-pair electron interactions. Interestingly, a significant negative resonance energy (5.4 kcal mol⁻¹) has been calculated for 1,4-dioxene (**4**).²⁶

Comparison of Dihydrodioxins (**1–4**), Oxacyclohexane (**5**), and Dioxacyclohexanes (**6–8**).

A comparison of the ring geometries of the unsaturated dihydrodioxins **1–4** and the chair conformations of oxacyclohexane (**5**, C_s), 1,2-dioxane (**6**, C₂),^{62–64} 1,3-dioxane (**7**, C_s),^{48,50,65–71} 1,4-dioxane (**8**, C_{2h})^{72–77} is also of interest. The half-chair conformer of 1,3-diox-4-ene (**3**) is 53.1, 54.6, and 3.4 kcal mol⁻¹, respectively, more stable than those of **1**, **2**, and **4** (Table I). Similarly, the chair conformer of 1,3-dioxane **7** is 50.3 and 5.8 kcal mol⁻¹, respectively, more stable than **6** and **7** (Table VII).

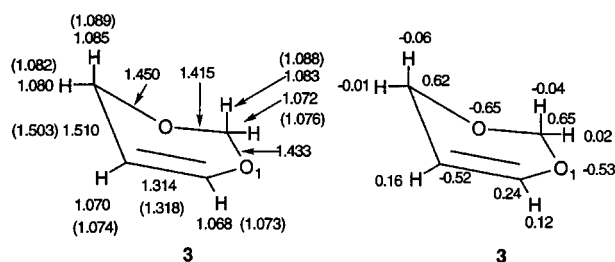
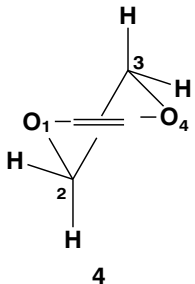


FIGURE 6. Calculated (3-21G) bond distances (Å) and electrostatic charges (electron) for 4H-1,3-dioxin (**3**). The 6-31G* bond distances (Å) are given in parentheses.

TABLE VI.
Calculated Dipole Moment and Geometry for 2,3-Dihydro-1,4-dioxin (4).



| | C ₂ , Half-Chair | | C _{2v} , Planar | | C _s , Boat | | Exptl ¹ |
|--|-----------------------------|--------|--------------------------|--------|-----------------------|--------|--------------------|
| | 3-21G | 6-31G* | 3-21G | 6-31G* | 3-21G | 6-31G* | |
| Bond length (Å) | | | | | | | |
| O ₁ —C ₂ | 1.445 | 1.405 | 1.442 | 1.404 | 1.447 | 1.407 | 1.400 |
| C ₂ —C ₃ | 1.528 | 1.519 | 1.567 | 1.552 | 1.562 | 1.548 | 1.523 |
| C ₅ =C ₆ | 1.313 | 1.318 | 1.307 | 1.311 | 1.308 | 1.313 | 1.338 |
| =C ₆ —O ₁ | 1.392 | 1.359 | 1.384 | 1.352 | 1.390 | 1.358 | 1.403 |
| =C—H | 1.066 | 1.071 | 1.066 | 1.070 | 1.066 | 1.071 | 1.09 |
| C ₂ —H _{ax} | 1.082 | 1.086 | | | | | |
| C ₂ —H _{eq} | 1.077 | 1.081 | 1.079 | 1.083 | 1.077 | 1.086 | 1.10 |
| Bond angle (°) | | | | | | | |
| O ₁ —C ₂ —C ₃ | 109.0 | 110.1 | 116.7 | 117.3 | 114.2 | 114.0 | |
| C ₃ —O ₄ —C ₅ = | 113.5 | 112.9 | 119.2 | 118.4 | 116.6 | 115.4 | |
| C ₅ =C ₆ —O ₁ | 123.1 | 123.5 | 124.2 | 124.4 | 121.2 | 120.5 | 123.4 |
| H—C ₂ —H | 110.3 | 109.1 | | | | | |
| Torsion angle (°) | | | | | | | |
| H _{eq} —C ₂ —C ₃ —H _{eq} | 63.1 | 62.4 | | | | | |
| H _{ax} —C ₂ —C ₃ —H _{ax} | 178.1 | 179.3 | 118.2 | 117.1 | 119.8 | 119.0 | |
| H—C ₅ =C ₆ —H | 1.9 | 2.2 | 0 | 0 | 0 | 0 | |
| O ₁ —C ₂ —C ₃ —O ₄ | 61.3 | 60.4 | 0 | 0 | 0 | 0 | |
| O ₄ —C ₅ =C ₆ —O ₁ | 2.3 | 1.6 | 0 | 0 | 0 | 0 | |
| C ₅ =C ₆ —O ₁ —C ₂ — | 14.9 | 14.9 | 0 | 0 | 33.1 | 36.6 | |
| =C ₆ —O ₁ —C ₂ —C ₃ | 45.4 | 44.0 | 0 | 0 | 30.8 | 34.2 | |
| Twist angle (°) | 29.4 | 28.1 | 0 | 0 | 0 | 0 | 29.9 |
| Dipole moment (debye) | 0.8 | 0.7 | 1.1 | 1.0 | 2.0 | 1.7 | 0.9 |

The 3-21G-calculated Csp³—O bond lengths in **1**, **2**, **5**, and **6** are 1.464 Å, 1.454 Å, 1.441 Å, and 1.458 Å, respectively. The 6-31G* calculated Csp³—O and O—O bond lengths in **1**, **2**, and **6** are approximately 0.07 Å and 0.05 Å, respectively, shorter than the 3-21G values (Tables III, IV, and VII).^{12,31–34} The 6-31G* calculated O—C—C—O torsion angles for **1**, **2**, and **6** are smaller than the 3-21G-computed values (Tables III, IV, and VII). The 3-21G-calculated O—C—C—O torsion angles for **1**, **2**, and **6** are 59.9°, 79.7°, and 75.7°, respectively. The relatively large value of 75.7° for **6** may suggest that its chair conformation is distorted toward a half-chair structure.^{62,63,78}

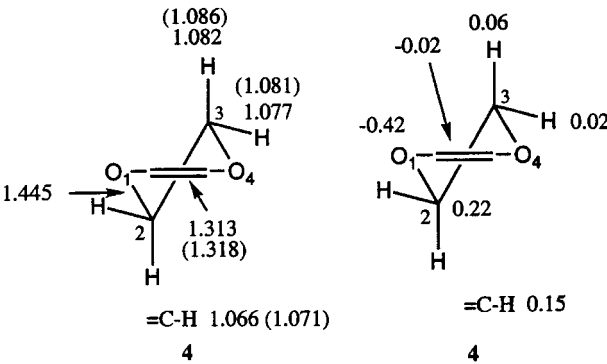
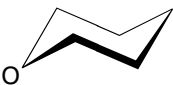
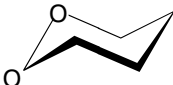
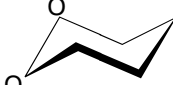



FIGURE 7. Calculated (3-21G) bond distances (Å) and electrostatic charges (electron) for 2,3-dihydro-1,4-dioxin (**4**). The 6-31G* bond distances (Å) are given in parentheses.

TABLE VII.

Calculated Energies and Geometries for Oxacyclohexane (5, C_s), 1,2-Dioxane (6, C_2), 1,3-Dioxane (7, C_s), and 1,4-Dioxane (8, C_{2h})^{a, b}

| |  |  |  |  |
|---|---|---|--|---|
| | 5 | 6 | 7 | 8 |
| Energy, hartree | | | | |
| 3-21G | −268.525601 | −304.068266 | −304.140521 | −304.129962 |
| MP2 / 3-21G // 3-21G | −269.091245 | −304.668770 | −304.727733 | −304.717483 |
| 6-31G* | −270.017907 | −305.745128 | −305.834498 | −305.825313 |
| MP2 / 6-31G* // 6-31G* | −270.842425 | −306.619615 | −306.699744 | −306.690439 |
| Energy difference, kcal mol ^{−1} | --- | 50.3 ^c (50.3) | 0.0 ^c (0.0) | 5.8 ^c (5.8) |
| Bond length (Å) ^d | | | | |
| O—O | | 1.463 (1.393) | | |
| O—C | 1.441 (1.401) | 1.458 (1.408) | | 1.444 (1.402) |
| O ₁ —C ₂ | | | 1.421 (1.384) | |
| O ₃ —C ₄ | | | 1.445 (1.404) | |
| Bond angles(°) ^d | | | | |
| O—O—C | | 105.6 (108.1) | | |
| O—C—C | 110.6 (111.4) | 108.8 (109.8) | | 109.2 (110.1) |
| O—C—O | | | 112.3 (112.5) | |
| C—O—C | 113.2 (113.6) | | 113.0 (112.8) | 111.7 (112.2) |
| Torsion angles (°) ^d | | | | |
| C—O—O—C | | 75.7 (73.9) | | |
| C—O—C—O | | | 60.4 (59.5) | |
| O—C—C—O | | | | 57.5 (55.8) |
| C—O—C—C | 60.1 (60.4) | | | |
| O—C—C—C | 56.5 (55.2) | | | |
| Dipole moment (debye) ^d | 1.9 (1.6) | 3.4 (2.9) | 2.6 (2.2) | 0.0 (0.0) |

^aOne hartree is 627.51 kcal mol^{−1}.

^bCalculations are for the chair conformations.

^cCalculated at the MP2 / 3-21G // 3-21 level. The calculated MP2 / 6-31G* // 6-31G* values are in parentheses.

^dCalculated at the 3-21G level. The calculated 6-31G* values are in parentheses.

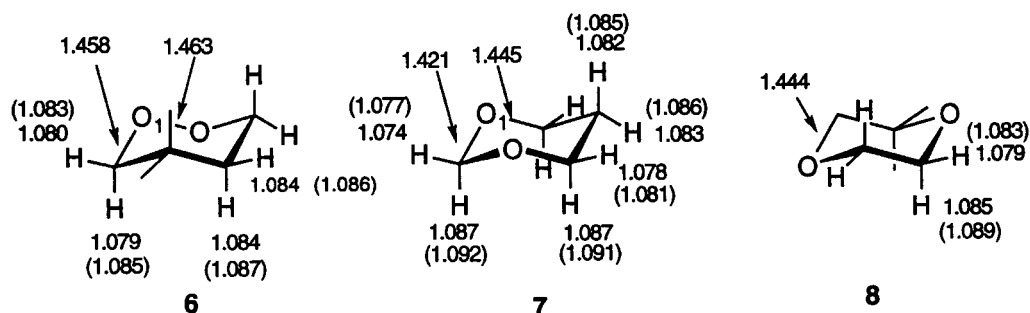


FIGURE 8. Calculated (3-21G) bond distances (Å) for 1,2-dioxane (6), 1,3-dioxane (7), and 1,4-dioxane (8). The 6-31G* bond distances (Å) are given in parentheses.

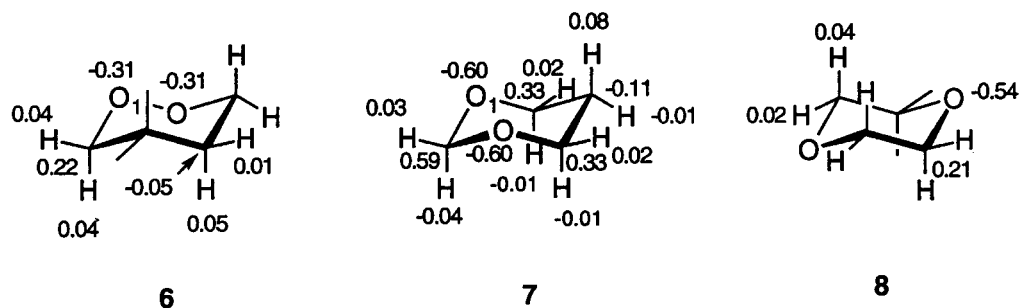


FIGURE 9. Calculated (3-21G) electrostatic charges (electron) for 1,2-dioxane (**6**), 1,3-dioxane (**7**), and 1,4-dioxane (**8**).

Structure **7** (1,3-dioxane) shows the influence of a $n_{O(1)} \rightarrow \sigma_{C(2)-H_{ax}}^*$ anomeric effect (Fig. 8). The axial C—H bonds are lengthened relative to the equatorial C—H bonds.^{48,68,79,80} The O—C—O bond angle (111.6°) in **3** is smaller than the O—C—O bond angle (112.3°) in **7**. The $Csp^3-O-Csp^3$ bond angle (113.6°) in **3** is larger than those in **5** (113.2°), **7** (113.0°), and **8** (111.7°). Figure 9 shows the calculated electrostatic charges for the dioxacyclohexanes **6**, **7**, and **8**.

In 1,4-dioxane (**8**), the calculated O—C—C—O torsion angle is 58° which is consistent with a half-chair conformation similar to the C_2 symmetric half-chair conformation of cyclohexene. Thus, in comparison with the 1,4-dioxane **8** (Table VII), the effect of the endocyclic double bond in **4** (Table IV) increases the O—C—C—O torsion angle by only 2–3°. The C—H_{ax} bond length in **8** is longer than the C—H_{eq} bond, which suggests a $n_{O(1)} \rightarrow \sigma_{C(2)-H_{ax}}^*$ anomeric interaction (Fig. 8). The C(2)—H_{ax} and C(4)—H_{ax} bond lengths in **5** are longer than the corresponding equatorial C—H bonds.⁸¹ The corresponding C—O and C—H bond lengths in **4**, **5**,^{50,81} and **8** are similar. It is also of interest to note that anomeric effects have been reported for substituted oxacyclohexanes (**5**)⁸² and substituted 1,4-dioxanes (**8**).⁸³

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